Fragrances from terpenes: a renewed heterogeneous hydroamination process

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- Location: Institut CEISAM, Nantes Université-CNRS, Nantes, France
- Level: Master (1st or 2nd year) or Engineer (4th or 5th year)
- 6 months between January-July 2026 (flexible starting date) - gratification of 610 €/month

Context

Biological feedstocks are an important sustainable alternative to petrochemicals. Terpenes (Figure 1) are widely available renewable substances non-competing with food. Among them, the β-myrcene represents an interesting model substrate for applying well-known olefin chemistry in catalysis.

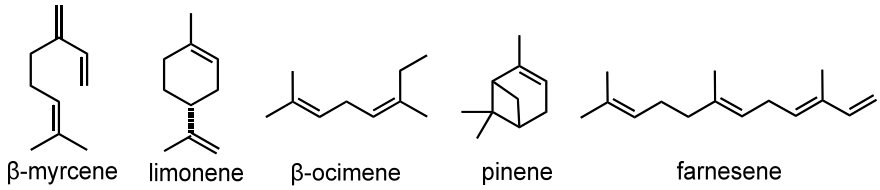
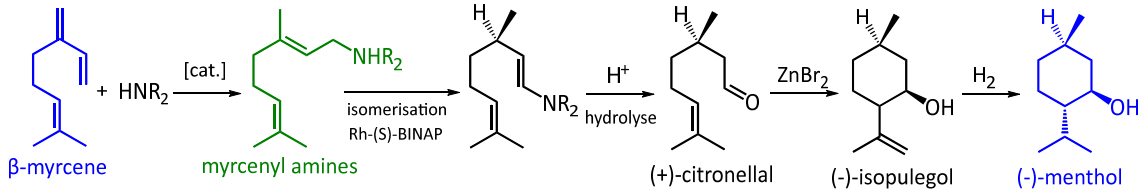


Figure 1. Examples of terpenes of interest

In this area, the sustainable catalytic hydroamination of alkenes and dienes allows the preparation of a large variety of alkylated amines with end applications in everyday life.[1] For instance, the hydroamination of terpenes affords terpenyl amines as useful precursors for the huge international trade of top-selling flavours and fragrances such as (-)-menthol (Scheme 1).[2]

Nowadays, the hydroamination of β-myrcene has only been industrialize by Takasago Perfumery Company (5000 t/y (-)-menthol), in the presence of Li metal catalyst, affording low catalytic activities (TOF = 12 h^{-1}). In the presence of *homogeneous* transition metal-based catalysts, this transformation gives improved catalytic activities but suffers from lower selectivitys and partial deactivation of the catalyst to inactive metal precipitate.



Scheme 1. Synthesis of (-)-menthol from terpenyl amines through the hydroamination of β-myrcene.

Objectives

The aim of this internship is to investigate the hydroamination of terpenes using heterogeneous catalysts. Thus, several transition metal-based catalysts will be prepared and then covalently graphed onto solid supports. The catalytic activity, as well as the leaching and recycling performance of the resulting assemblies, will be tested in the hydroamination of β-myrcene. In the frame of this project, the Master student will:

- Synthesize, isolate and characterize organic and organometallic compounds, including a) nitrogen, phosphorous and NHC containing ligands and b) their organometallic complexes with metal precursors.
- Graft the ligands/complexes onto commercial solid supports and characterize the new catalyst.
- Evaluate (screening and optimisation) the catalytic properties, the leaching and the recycling of the novel catalytic systems in the hydroamination of myrcene.

Bibliographic references

1. J.-J. Brunet, D. Neibecker, in *Catalytic Hetero-functionalization,* Wiley-VCH, Germany, **2001**, pp. 91-141;
2. A. Behr, L. Johnen, *ChemSusChem* **2009**, *2*, 1072; H. Kumobayashi, S. Mitsuhashi, S. Akutagawa, S. Ohtsuka, *Chem. Lett*. **1986**, *15*, 157; Behr, L. Johnen, N. Rentmeister, *Adv. Synth. Catal.* **2010**, *352*, 2062-2072; D. Vogelsang, J. M. Dreimann, D. Wenzel, L. Peeva, J. da Silva Burgal, A. G. Livingston, A. Behr, A. J. Vorholt, *Ind. Eng. Chem. Res.* **2017**, *56*, 13634-13641; R. Schulz, L. Sengen, K. Giebelmann, S. Hunold, T. Zeiner, *Chem. Ing. Tech.* **2018**, *90* 947-955
3. M. Rodriguez-Zubiri, C. Baudequin, A. Béthegnies, J.-J. Brunet, *ChemPlusChem* **2012**, *77*, 445; J.-J. Brunet, N.-C. Chu, M. Rodriguez-Zubiri, *Eur. J. Inorg. Chem.* **2007**, 4711.